57Fe ABSORPTION AND EMISSION SPECTROSCOPY IN SOME COBALT ACETYLACETONATE COMPLEXES [Co (acac)3, Co (acac)2, Co (acac)2×2H2O]

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In diamagnetic $Co(acac)_3$ the ^{57}Fe absorber impurities (0.5 - 3 at.%) occur uniquely in the high spin Fe^{3+} configuration, with paramagnetic relaxation effects between 1.5 and 190 K. The ^{57}Fe emission spectra (fig. 1) reveal the coexistence of both Fe^{2+} and Fe^{3+} ions in their high-spin configurations. Part of the Fe^{3+} component (60 ± 5 % of the area from 4.2 to 190 K) is split by paramagnetic relaxation whereas another part is not affected by these effects and shows up merely as a doublet (20 ± 5 % of the total area). The Fe^{2+} quadrupole doublet represents 20 ± 5 % of the total area.

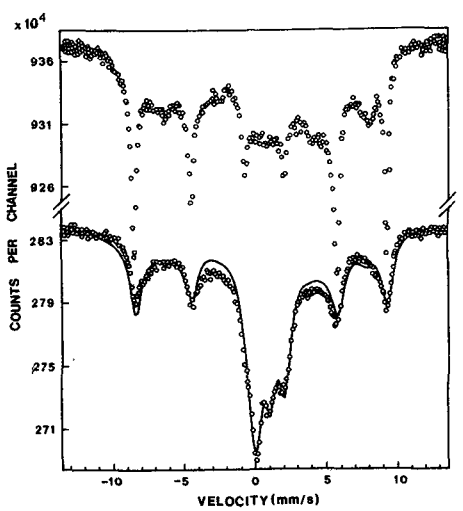

Fig. 1 : Absorption (top) and emission spectra of $Co(acac)_3$ at 4.2 K.

In anhydrous $Co(acac)_2$, the ^{57}Fe absorber impurities occur as high-spin Fe^{2+} ions with two sets of different hyperfine interaction parameters (fig. 2) corresponding to the non-equivalent crystallographic sites occurring in this complex /1/.

Paramagnetic relaxation effects are observed for the Fe^{2+} ions below ~ 30 K and are investigated as a function of temperature and of applied magnetic field. They characterize the occurrence of a doublet spin-orbit ground state arising from the perturbation of a well isolated orbital singlet. The ^{57}Fe emission spectra in $Co(acac)_2$ reveal also the two preceeding unequivalent Fe^{2+} sites, in addition to a new Fe^{2+} doublet and an Fe^{3+} component. The relative spectral intensities are equal at 77 and 150 K (65 ± 3 % for the normal Fe^{2+} ions, 10 ± 3 % for the new Fe^{2+} component and 25 ± 3 % for the Fe^{3+} component). They cannot be determined at 4.2 K because of the paramagnetic relaxation effects. The resonance widths were investigated as a function of the absorber thickness and were found to be natural for the regular Fe^{2+} components (W_{exp} = 0.30 mm/s) whereas both the new Fe^{2+} and Fe^{3+} components are significantly broadened.

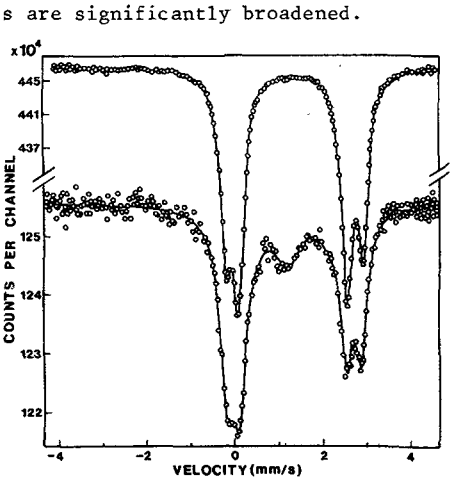

Fig. 2 : Absorption (top) and emission spectra of $Co(acac)_2$ at 77 K.

In $Co(acac)_2.2H_2O$, the absorption ^{57}Fe spectra reveal a single Fe^{2+} pattern (fig. 3) in the high spin state. The emission spectra reveal both at 4.2 and 77 K a new Fe^{2+} component (20 ± 3 % of the spectral area) and an Fe^{3+} component (17 ± 3 %) in addition to the regular Fe^{2+} ions (63 ± 3 %) ; the latter present unbroadened resonance widths whereas the two other components are significantly broadened.

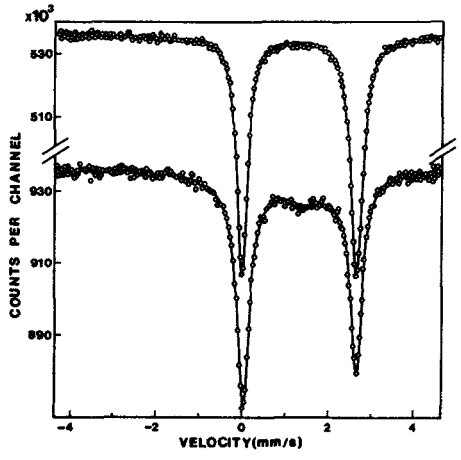

Fig. 3 : Absorption (top) and emission spectra of $Co(acac)_2.2H_2O$ at 4.2 K.

In the three source hosts under investigation the ^{57}Fe atoms created by EC decay from ^{57}Co, are observed partially in their normal electronic and structural configuration, defined as corresponding to that of the ^{57}Fe absorber impurities. The resonance lines corresponding to these normal ions are unbroadened and are therefore attributed to simple substitutional sites in unperturbed molecular environments. In all three complexes we observe the additional stabilization of both isovalent iron decay products in perturbed structural environments and aliovalent iron species, i.e. Fe^{2+} ions in $Co(acac)_3$ and Fe^{3+} ions in $Co(acac)_2$ and $Co(acac)_2.2H_2O$. These spectral components are significantly broadened, due likely to a distribution of hyperfine interactions at these sites. In diamagnetic $Co(acac)_3$, the anomalous isovalent Fe^{3+} ions do not present the expected paramagnetic relaxation phenomenon. The features observed in the source experiments can be understood in the frame of the self-radiolysis model developed previously to account for the after-effects of the EC decays. Paramagnetic relaxation effects would be suppressed for those Fe^{3+} ions in the vicinity of paramagnetic centers created as a consequence of the local self-radiolysis by the Auger electrons and X-rays, because of the enhanced spin-spin interactions /2/. The stabilization of reduced aliovalent species in $Co(acac)_3$ is consistent with the radiolytic reduction simulated in this host by an external irradiation /3/ at a dose comparable to that of the internal self-irradiation. The observation of new isovalent iron in $Co(acac)_2$ and $Co(acac)_2.2H_2O$ agrees also with this model, the nature of the aliovalent states being determined by competing acceptor-donor reactions between the radiolytic fragments and the isovalent Fe decay charge state.

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References

/1/ Cotton, F.A. and Elder, R.C., Inorg. Chem. 4 (1965) 1145

/2/ Friedt, J.M., Shenoy, G.K. and Abstreiter, G., Intern. Conf. Applic. Mössb. Effect, Israël (1972)

/3/ Baggio-Saitovitch, E., Friedt, J.M. and Danon, J., J. Chem. Phys. 56 (1972) 1269.